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### (54) COMPOSITION FOR REFRIGERATOR WORKING FLUID

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a compsn. for refrigerator working fluids, which contains a refrigerator oil based on a specific ester and a hydrofluorocarbon mixture contg. a specified amt. of difluoromethane and in which the refrigerator oil and the mixture are compatible with each other.

SOLUTION: This compsn. contains a refrigerator oil (A) based on an ester which is obtd. by reacting a 1-10C linear and/or branched monohydric alcohol (e.g. n-butanol) with an arom. tribasic acid (e.g. trimellitic acid) or its anhydride and has an acid value of 1mgKOH/g or lower, a hydroxyl value of 10mgKOH/g or lower, an iodine value of 10 or lower, and a kinematic viscosity at 40°C of 25-150mm<sup>2</sup>/s and a hydrofluorocarbon mixture (B) which contains 45wt.% or higher difluoromethane and pref. comprises 45-70wt.% difluoromethane and 30-55wt.% pentafluoroethane. The compounding ratio of B to A is pref. (20/1)-(1/10), though not specifically limited.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] the refrigerator actuation style this invention excelled [ style ] in the compatibility of refrigerating machine oil and mixed hydro fluorocarbon -- the body and its function -- it is related with a constituent.

[0002]

[Description of the Prior Art] Recently, as for the dichlorodifluoromethane (CFC12) currently used for the refrigerator or the car air conditioner for the ozonosphere protection, use was forbidden in 1995. Then, use regulation of the chlorodifluoromethane (HCFC22) currently used for the room air conditioner, the packaged air conditioner, the industrial refrigerator, etc. started. Therefore, the hydro fluorocarbon, 1, 1, and 1, which does not destroy an ozone layer, 2-tetrafluoro ethane (HFC134a), difluoromethane (HFC32), and pentafluoro ethane (HFC125) are developed as a substitute of this dichlorodifluoromethane and chlorodifluoromethane. [ for example, ]

[0003] These hydro fluorocarbon has the bad compatibility of these lubricating oils and hydro fluorocarbon, when lubricating oils, such as naphthene straight mineral oil currently generally conventionally used as refrigerating machine oil since the polarity is high, and the Pori alpha olefin, alkylbenzene, are used compared with a dichlorodifluoromethane or chlorodifluoromethane, and two-phase separation is started in low temperature. If two-phase separation is started, oil return worsens, a thick oil film will adhere near the condenser as a heat exchanger, or an evaporator, and heat transfer will be barred, and it will become the cause of important defects, such as poor lubrication and foaming at the time of starting. Therefore, conventional refrigerating machine oil cannot be used as refrigerating machine oil under these new hydro fluorocarbon existences.

[0004] Therefore, now, base oil, such as the above-mentioned hydro fluorocarbon, a dissolving polyalkylene glycol, and ester, a carbonate, is used for refrigerating machine oil.

[0005] 1, 1, 1, and 2-tetrafluoro ethane is actually used for the refrigerator as ester base oil and hydro fluorocarbon as refrigerating machine oil. Moreover, ester base oil is evaluated by the room air conditioner, the packaged air conditioner, the industrial refrigerator, etc. as refrigerating machine oil.

[0006] However, in the field for which the conventional chlorodifluoromethanes, such as a room air conditioner, a packaged air conditioner, and an industrial refrigerator, were used, the mixed hydro fluorocarbon which contains difluoromethane as hydro fluorocarbon is evaluated from a viewpoint of frozen effectiveness. However, if difluoromethane is used, compatibility with ester base oil will worsen compared with 1, 1, 1, and 2-tetrafluoro ethane, and two-phase separation will be started in low temperature. Especially the ratio of difluoromethane becomes remarkable at 45 % of the weight or more. Since oil return worsens as it mentioned above, when two-phase separation happened, a thick oil film adheres near the condenser as a heat exchanger, or an evaporator, and heat transfer is barred and it becomes the cause of important defects, such as poor lubrication and foaming at the time of starting, a refrigerator actuation style with sufficient compatibility with the mixed hydro fluorocarbon containing the difluoromethane in low temperature -- the body and its function -- the refrigerator actuation style

dissolved below -20 degrees C with the room air conditioner and packaged air conditioner using a constituent especially a rotary mold, a scroll type, and a screw mold compressor, or an industrial refrigerator -- the body and its function -- the constituent is demanded.

[0007] the refrigerator actuation style which makes base oil the ester obtained from trimellitic acid and monohydric alcohol at JP,4-226193,A -- the body and its function -- although the constituent is indicated, there is no publication of trimellitic acid ester in an example, and reference is not made at all about difluoromethane.

[0008] Although the constituent for refrigerator working fluids which consists of mixed hydro fluorocarbon which contains difluoromethane in JP,5-17789,A, JP,5-32985,A, JP,5-239480,A, JP,6-9978,A, and JP,6-17073,A as the refrigerating machine oil which makes hindered ester base oil is indicated, difluoromethane has not made reference at all about compatibility with 45% of the weight or more of mixed hydro fluorocarbon.

[0009] Although the compatibility of the mixed hydro fluorocarbon and ester base oil which become JP,6-184575,A from 40 % of the weight of difluoromethane and 60 % of the weight of pentafluoro ethane is indicated, ester base oil and difluoromethane have not made reference at all about compatibility with 45% of the weight or more of mixed hydro fluorocarbon.

[0010]

[Problem(s) to be Solved by the Invention] therefore, the refrigerating machine oil with which the purpose of this invention makes ester base oil and the refrigerator actuation style difluoromethane excelled [ style ] in the compatibility of the refrigerating machine oil and the mixed hydro fluorocarbon which come to contain 45% of the weight or more of mixed hydro fluorocarbon -- the body and its function -- it is in offering a constituent.

[0011]

[Means for Solving the Problem] the refrigerator actuation style in which difluoromethane contains 45% of the weight or more of mixed hydro fluorocarbon by using the refrigerating machine oil which makes specific ester base oil as a result of repeating research wholeheartedly, in order that this invention persons may solve said technical problem -- the body and its function -- a header and this invention were completed for the ability of a constituent to solve said technical problem.

[0012] Namely, summary of this invention [1] Monohydric alcohol of the straight chain of 1 carbon atomic numbers 1-10, and/or branched chain, The refrigerating machine oil which makes base oil the ester obtained from the acid anhydride of the tribasic acid which has a ring, or this tribasic acid, And the mixed hydro fluorocarbon which contains 2 difluoromethane (HFC32) 45% of the weight or more, the refrigerator actuation style characterized by containing -- the body and its function -- a constituent and [2] Mixed hydro fluorocarbon the refrigerator actuation style of the aforementioned [1] publication which is mixed hydro fluorocarbon which furthermore contains pentafluoro ethane (HFC125) -- the body and its function -- a constituent -- [3] a refrigerator actuation style the above [1] whose carbon atomic numbers of the ring of the acid anhydride of the tribasic acid which has a ring, or this tribasic acid are 9-12, or given in [2] -- the body and its function -- a constituent -- [4] aforementioned [1]- [3] whose acid anhydride of the tribasic acid which has a ring, or this tribasic acid is trimellitic acid or trimellitic anhydride -- either -- the refrigerator actuation style of a publication -- the body and its function -- a constituent -- [5] 50/50 (% of the weight) of mixed hydro fluorocarbon sets [ refrigerating machine oil / the ratio of 30 volume %, and difluoromethane / pentafluoro ethane ] on the conditions of 70 volume %. aforementioned [1]- [4] whose low-temperature two-phase separation temperature is -20 degrees C or less -- either -- the refrigerator actuation style of a publication -- the body and its function - a constituent -- [6] aforementioned [1]- [5] whose kinematic viscosity in 40 degrees C of ester is 25-150mm<sup>2</sup> / s -- either -- the refrigerator actuation style of a publication -- the body and its function -- it is related with a constituent.

[0013]

[Embodiment of the Invention]

1. The refrigerating machine oil used for this invention about refrigerating machine oil is refrigerating machine oil which makes base oil the ester obtained from the monohydric alcohol (component -1) of the

straight chain of the carbon atomic numbers 1-10, and/or branched chain, and the acid anhydride (component -2) of the tribasic acid which has a ring, or this tribasic acid.

[0014] \*\* The carbon atomic numbers of the monohydric alcohol of the straight chain of a component -1 and/or branched chain are 1-10 about a component -1, and it is 1-8 preferably, is 1-6 still more preferably, and is 1-4 especially preferably. As for the viewpoint in which the ester obtained has suitable viscosity, and the viewpoint of compatibility with difluoromethane content mixing hydro fluorocarbon to a carbon atomic number, ten or less are desirable. As an example of the alcohol of a component -1, a methanol, ethanol, n-propanol, 1-methylethanol, n-butanol, 2-methyl propanol, n-pentanol, n-hexanol, n-heptanol, 3-methyl hexanol, 5-methyl hexanol, n-octanol, 2-ethylhexanol, n-nonanol, 3 and 5, a 5-trimethyl hexanol, n-decanol, etc. are mentioned. A methanol, n-butanol, 2-methyl propanol, 3-methyl hexanol, 5-methyl hexanol, 2-ethylhexanol, 3 and 5, and especially a 5-trimethyl hexanol are excellent from a viewpoint of compatibility with difluoromethane content mixing hydro fluorocarbon in these.

[0015] \*\* A component -2 has the desirable tribasic acid in which the ester obtained has a ring from the viewpoint which has suitable viscosity, and a viewpoint of compatibility with difluoromethane content mixing hydro fluorocarbon about a component -2. as the tribasic acid which has the ring of a component -2 -- from a viewpoint of compatibility with difluoromethane content mixing hydro fluorocarbon -- desirable -- the ring of the carbon atomic numbers 9-12 -- they are the ring of the carbon atomic numbers 9-10, and the tribasic acid which has the ring of the carbon atomic number 9 preferably especially more preferably. From a viewpoint of the thermal stability of refrigerating machine oil, a hemi merit acid, trimesic acid, and trimellitic acid are desirable, and, specifically, trimellitic acid is more desirable from a viewpoint of availability. Moreover, since reactivity increases [ the direction which uses an acid anhydride for manufacture of ester ], the acid anhydride of the above-mentioned tribasic acid is also mentioned as a suitable example of a component -2. The ester used for this invention can be obtained from one or more kinds and one or more kinds of the tribasic acid which has the ring of a component -2, or an acid anhydride of the alcohol of a component -1 by the well-known esterification reaction and well-known ester exchange reaction which are usually performed.

[0016] As an example of this ester, the ester of a methanol and trimellitic acid, n-butanol, the ester of trimellitic acid and 2-methyl propanol, and the ester of trimellitic acid, n-butanol, 2-methyl propanol, and the ester of trimellitic acid, n-butanol, 2-ethylhexanol, and the ester of trimellitic acid, 2-methyl propanol, 2-ethylhexanol, and the ester of trimellitic acid, n-butanol, a 3, 5, and 5-trimethyl hexanol, the ester of trimellitic acid and 2-methyl propanol, a 3, 5, and 5-trimethyl hexanol, the ester of trimellitic acid, etc. are mentioned. In addition, the refrigerating machine oil used for this invention may make this ester base oil, and may use two or more kinds of ester for this refrigerating machine oil.

[0017] Although especially the acid number of the ester used in this invention is not limited, 1 or less mgKOH/g is desirable from a viewpoint which controls the corrosion of a metallic material, a wear-resistant fall, the fall of thermal stability, and the fall of electric insulation, 0.2 or less mgKOH/g is more desirable, 0.1 or less mgKOH/g is still more desirable, and especially 0.05 or less mgKOH/g is desirable. Here, the acid number is JIS. It can measure by the approach of K-2501.

[0018] From a viewpoint of the hygroscopicity of refrigerating machine oil, and thermal stability, the hydroxyl value of the ester used for this invention has 10 or less desirable mgKOH/g, its 8 or less mgKOH/g is more desirable, its 5 or less mgKOH/g is still more desirable, especially its 3 or less mgKOH/g is desirable, and its 1 or less mgKOH/g is the most desirable. Here, a hydroxyl value can be measured by the approach of JISK-2501.

[0019] Although especially the iodine number (Img / 100g) of the ester used for this invention is not limited, ten or less are desirable from a viewpoint of the thermal oxidation stability of ester, five or less are more desirable, three or less are still more desirable, and one especially or less is desirable. Here, the iodine number is JIS. It can measure by the approach of K-3211.

[0020] From energy-saving nature, sealing nature, and a wear-resistant viewpoint, the kinematic viscosity in 40 degrees C of the ester used for this invention has the desirable range of 25-150mm<sup>2</sup>/s, its range of 30-100mm<sup>2</sup>/s is more desirable, its range of 40-80mm<sup>2</sup>/s is still more desirable, and especially its range of 50-75mm<sup>2</sup>/s is desirable. Here, kinematic viscosity is measured by the approach of JISK-

2283. In the refrigerating machine oil which makes the ester in this invention base oil, straight mineral oil, the Pori alpha olefin, alkylbenzene, ester and the polyethers other than the above, the perfluoro ether, phosphoric ester, etc. may be mixed in the range which does not spoil compatibility with difluoromethane content mixing hydro fluorocarbon. In addition, the ester in this invention is a thing of the lubricating oil which uses as base oil and is blended with refrigerating machine oil which occupies 80 % of the weight or more preferably 50% of the weight or more.

[0021] The ratio of difluoromethane / pentafluoro ethane can add and use various lubricating oil additive, such as the antioxidant usually used, an extreme pressure agent, an oiliness improver, a defoaming agent, a detergent dispersant, a rust-proofer, a demulsifier, a viscosity index regulator, a metal deactivator, and a pour point depressant, for the refrigerating machine oil which makes the ester in this invention base oil in the range which does not spoil compatibility with 45/55% of the weight or more of mixed hydro fluorocarbon.

[0022] 2. The mixed hydro fluorocarbon used for this invention about mixed hydro fluorocarbon contains difluoromethane 45% of the weight or more. It is mixed hydro fluorocarbon which contains pentafluoro ethane further more preferably. From a viewpoint of frozen effectiveness and safety, the desirable rate of a compounding ratio has 45 - 70 desirable % of the weight, and 45 - 60 % of the weight of difluoromethane is [ a rate ] still more desirable. Pentafluoro ethane has 30 - 55 desirable % of the weight, and its 40 - 55 % of the weight is still more desirable. As one of the most desirable rates of a compounding ratio, 50 % of the weight of difluoromethane and 50 % of the weight of pentafluoro ethane are mentioned.

[0023] 3. a refrigerator actuation style -- the body and its function -- the refrigerator actuation style of this invention which was excellent in the compatibility of refrigerating machine oil and mixed hydro fluorocarbon about the constituent -- the body and its function -- a constituent contains the refrigerating machine oil which makes the above ester base oil, and the mixed hydro fluorocarbon containing difluoromethane. The constituent for refrigerator working fluids of this invention is the the best for a rotary mold, a scroll type, and a screw mold compressor. It is suitable for using for compressors, such as a room air conditioner, a packaged air conditioner, and an industrial refrigerator, in application.

[0024] In the constituent for refrigerator working fluids of this invention, especially the rate of a compounding ratio of refrigerating machine oil and mixed hydro fluorocarbon is not limited, and its mixed hydro fluorocarbon / refrigerating-machine-oil = 20 / 1 - 1/10-fold quantitative ratio are desirable, for example, its 10 / 1 - 1/5-fold quantitative ratio are more desirable, and especially 5 / 1 - 1/5 are desirable. the above from a viewpoint which acquires sufficient refrigerating capacity -- a mixing ratio is 1/10 or more -- desirable -- a refrigerator actuation style -- the body and its function -- it is desirable that it is 20/1 or less from a viewpoint which makes viscosity of a constituent suitable.

[0025] The constituent for refrigerator working fluids of this invention is excellent in the compatibility of refrigerating machine oil and mixed hydro fluorocarbon. The approach shown below can estimate the property which the constituent for refrigerator working fluids requires. That is, refrigerating machine oil evaluates [ the ratio of 30 volume %, and difluoromethane / pentafluoro ethane / 50/50 (% of the weight) of mixed hydro fluorocarbon ] by measuring low-temperature two-phase separation temperature in the conditions of 70 volume %. the case where low-temperature two-phase separation temperature is measured on these conditions -- the refrigerator actuation style of this invention -- the body and its function -- it is still more desirable that it is -10 degrees C or less, as for this temperature of a constituent, it is desirable that it is 10 degrees C or less, and it is [ it is more desirable that it is 0 degree C or less, and / it is desirable that it is especially -20 degrees C or less, and ] most desirable that it is -30 degrees C or less.

[0026] In the constituent for refrigerator working fluids of this invention, the following additives may be added suitably.

(i) -- the refrigerator actuation style of this invention excellent in the compatibility of refrigerating machine oil and mixed hydro fluorocarbon -- the body and its function -- the additive from which water is removed may be added to a constituent. Additives, such as a compound which has an epoxy group as an additive from which water is removed, and ortho ester, an acetal (ketal), a carbodiimide, are

mentioned.

[0027] (ii) -- the refrigerator actuation style of this invention which was excellent in the compatibility of refrigerating machine oil and mixed hydro fluorocarbon again -- the body and its function -- to a constituent, the metal deactivator which has the phenol system compound which has the radical trap ability for raising thermal stability, and chelate ability may be added.

[0028]

[Example] Hereafter, although the example of manufacture and an example explain this invention in more detail, this invention is not limited at all by these examples etc.

the 11. 4 opening flask furnished with the example agitator of manufacture, a thermometer, nitrogen entrainment tubing, and dehydration tubing with a condensator -- 2-methyl propanol 260.2g (3.5 mols) and 150.0g (0.78 mols) of trimellitic anhydride -- in addition, the ordinary pressure reaction was performed at 118 degrees C under the nitrogen air current for 10 hours. Thus, the obtained ester was refined and it considered as refrigerating machine oil A. Moreover, the same reaction as the above was performed and refrigerating-machine-oil B-F used for this invention shown in Table 1 and refrigerating-machine-oil a-h used for the comparison article shown in Table 2 were obtained.

[0029] The presentation of the mixed hydro fluorocarbon (hydro fluorocarbon 1-3) used for an example is as follows.

Hydro fluorocarbon 1HFC32/HFC125 (50/50 % of the weight)

Hydro fluorocarbon 2HFC32/HFC125 (45/55 % of the weight)

Hydro fluorocarbon 3HFC32/HFC125 (40/60 % of the weight)

[0030] 30 volume % and hydro fluorocarbon 1, 2, and 3 measured [ 40-degree-C kinematic viscosity (JIS K-2283) of the refrigerating machine oil obtained in the example of example manufacture, and refrigerating machine oil ] the two-phase separation temperature in the conditions of 70 volume %. The result is shown in Table 1. Moreover, the result similarly measured using the refrigerating machine oil of a comparison article is shown in Table 2.

[0031]

[Table 1]

	冷凍機油		40℃動粘度 (mm <sup>2</sup> /s)	二相分離温度 (℃、30vol% *)		
	1 価アルコール	酸/酸無水物		ハイドロフルオロカーボン 1	ハイドロフルオロカーボン 2	ハイドロフルオロカーボン 3
A	2-メチルプロパノール	トリメチット酸無水物	81.9	< -60	< -60	< -60
B	n-ブタノール	トリメチット酸無水物	26.1	-56	< -60	< -60
C	メタノール	トリメチット酸無水物	92.5	< -60	< -60	< -60
D	n-ブタノール/2-メチルプロパノール =30/70wt%	トリメチット酸無水物	46.8	< -60	< -60	< -60
E	2-メチルプロパノール/2-エチルヘキサノール =80/20wt%	トリメチット酸無水物	66.8	-35	-47	< -60
F	2-メチルプロパノール/3, 5, 5-トリメチルヘキサノール =80/20wt%	トリメチット酸無水物	67.1	-40	-51	< -60

\* 冷凍機作動流体用組成物中の冷凍機油の体積%

[0032]

[Table 2]

	冷凍機油		40℃動粘度 (mm <sup>2</sup> /s)	二相分離温度 (°C、30vol% *)		
	アルコール	酸/酸無水物		ハイドロフルオロカーボン1	ハイドロフルオロカーボン2	ハイドロフルオロカーボン3
a	iso-トリチanol	トリリット酸無水物	209.3	> 0	> 0	> 0
b	2-メチルプロパノール	フタル酸無水物	14.1	< -60	< -60	< -60
c	2-エチルヘキサンール	フタル酸無水物	26.9	> 0	> 0	> 0
d	n-ブタノール	ピコリット酸無水物	常温 固体	測定不能	測定不能	測定不能
e	2-メチルプロパノール	ピコリット酸無水物	常温 固体	測定不能	測定不能	測定不能
f	n-オクタノール	ピコリット酸無水物	71.7	> 0	> 0	> 0
g	ペンタエリスリトール	2-エチルヘキサン酸	44.8	> 0	> 0	-5
h	ペンタエリスリトール	2-メチルヘキサン酸	28.8	-19	-26	-36

\* 冷凍機作動流体用組成物中の冷凍機油の体積%

[0033] The above-mentioned result showed that each this invention article was excellent in compatibility. Even if it used the hydro fluorocarbon 1 and 2 to which especially compatibility worsens, compatibility was -20 degrees C or less. The comparison article d and e is a solid-state in ordinary temperature, and it turned out that the comparison article b has low 40-degree-C kinematic viscosity, and it is hard to use it as refrigerating machine oil. moreover, the refrigerator actuation style in the comparison article using refrigerating machine oil a, c, f, g, and h -- the body and its function -- each compatibility of a constituent was a thing inferior to this invention article. the refrigerator actuation style using the mixed hydro fluorocarbon which contains difluoromethane from this -- the body and its function -- in a constituent, when using ester as refrigerating machine oil, it turns out that compatibility changes notably with structures of this ester.

[0034]

[Effect of the Invention] the refrigerator actuation style which was excellent in the compatibility of refrigerating machine oil and mixed hydro fluorocarbon with this invention even if difluoromethane contains 45% of the weight or more of mixed hydro fluorocarbon -- the body and its function -- it became possible to offer a constituent.

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[Translation done.]